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Size Distributions of Species in Fine Particles in Denver Using a Microorifice Impactor

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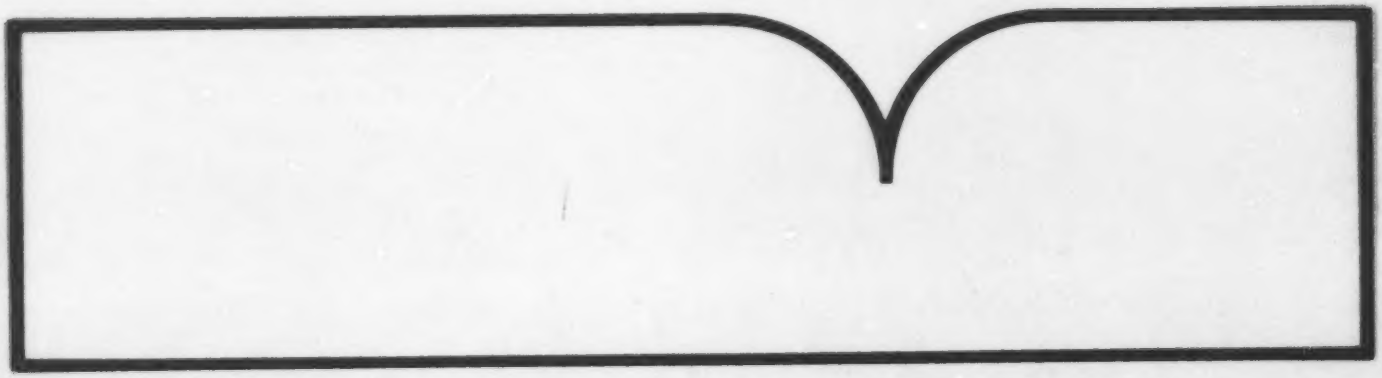

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16. ABSTRACT

Size fractionated fine particles in Denver, Colorado, were collected by a microorifice impactor and analyzed for mass and elemental composition by a beta-gauge and an X-ray fluorescence spectrometer. A least squares procedure was used to fit a log normal distribution function to the data in order to determine values and uncertainties for the mass median diameter and geometric standard deviation. The validity of the uncertainties so determined was tested by comparing them to uncertainties derived from Monte Carlo simulations.

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JOURNAL ARTICLE

Size Distributions of Species in Fine Particles in Denver Using a Microorifice Impactor

Hashima Hasan* and Thomas G. Dzubay
Atmospheric Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Size-fractionated fine particles in Denver, Colorado, were collected by a microorifice impactor and analyzed for mass and elemental composition by a β-gauge and an X-ray fluorescence spectrometer. A least-squares procedure was used to fit a lognormal distribution function to the data in order to determine values and uncertainties for the mass median aerodynamic diameter and geometric standard deviation. The validity of the uncertainties so determined was tested by comparing them to uncertainties derived from Monte Carlo simulations.

INTRODUCTION

Although X-ray fluorescence (XRF) has been shown to be a useful technique for quantitative determination of elemental concentrations in filter-collected aerosol samples (Stevens et al., 1978), it has not been useful in analyzing samples collected by conventional cascade impactors. This is a consequence of a characteristic of XRF spectrometers that causes the sensitivity to vary with position across a sample. That characteristic limits the application of XRF to cases for which the unknown samples and calibration standards have the same density profile. Because such a condition can be met conveniently only when the samples and standards have uniform density profiles, XRF has been applied only to uniformly deposited filter samples. Consequently, XRF analysis of aerosol size distributions has often been limited to analysis of the two fractions collected on filters by a dichotomous sampler.

The microorifice impactor, a recent innovation in the design of multistage cascade impactors, produces uniform deposits of submicrometer-sized particles (Kuhlmey et al, 1981; Marple et al., 1981; Marple and Rubow, 1984). Each impactor stage consists of a thin metal plate having a large number of round holes, which serve as jets that impinge air onto a collection surface. During sampling, the collection surfaces rotate continuously; this causes particles to be deposited uniformly in concentric rings.

We operated a microorifice impactor in Denver, Colorado, in order to collect submicrometer-sized particles in four size ranges. The samples were analyzed for mass and element concentrations by a β-gauge and by XRF. To test the validity of the analytical results, we compared the sum of the impactor stage results with results from an adjacent dichotomous sampler, which was operated during a study of the "Denver Brown Cloud" (Lewis and Stevens, 1984). Then we used a least-squares fitting procedure to determine the parameters of a lognormal distribution function that represents the impactor data. Error estimates for the parameters were also derived during the least-squares analysis, and we tested the validity of the error estimates by use of Monte Carlo simulations.

*National Research Council Resident Research Associate. Present address: Space Telescope Science Institute, 3700 San Martin Dr., Baltimore, MD 21218.

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EXPERIMENTAL PROCEDURE

The sampling site was located 10 km northeast of downtown Denver at the Mile High Kennel Club. Samples were collected in the microorifice impactor for 11.5-h periods that began each day at about 06:00 and 18:00 MST (Mountain Standard Time; add 7 h to obtain universal time) from January 11 to 19, 1982. Samples of 12-h duration that began at 06:00 and 18:00 MST were collected by an adjacent dichotomous sampler.

Particles were collected on four impaction stages in the microorifice impactor; the characteristics of these stages are given in Table 1. The initial impaction stage, stage A, was used to eliminate coarse particles. Its impaction surface was not analyzed but was wiped clean and coated with petroleum grease at the start of each sampling period. To prevent the greased surface from becoming excessively coated with large dust particles, a cyclone was attached at the inlet; this allowed only particles smaller than 3 μm to enter the impactor. The impaction surfaces for stages B, D, and F were 2-μm-pore-size Teflon filters (Membrana Corp., Pleasanton, CA). A backup 2-μm-pore-size Teflon filter attached at the outlet of the impactor collected particles not deposited on the earlier stages. Deposit areas were 7.5 cm^2 for the impactor stages and 8.2 cm^2 for the backup filter. The flow rate of the air entering the impactor was measured at the start and end of each sampling period by using a Singer Model 115 dry test meter. The initial and final values were in the ranges of 30.0 ± 0.1 and 29.7 ± 1.0 liters/min, respectively. The pressure drop across the four impactor stages was 31 cm of water.

Mass concentrations were determined by β-ray attenuation by an instrument and procedures described by Jaklevic et al. (1981). Courtney et al. (1982) have shown that bias relative to gravimetric mass measurements is small. Elemental concentrations were determined by an energy dispersive XRF spectrometer developed by Jaklevic et al. (1976). Sulfur (S) calibration was based on thin, gravimetrically analyzed ammonium sulfate aerosol deposits; calibration for other elements was based on standards consisting of vapor-deposited films (Micromatter Co., Eastsound, WA). The XRF spectra were analyzed by a least-squares fitting method that used stored reference spectra (Drane et al., 1980).

SIZE DISTRIBUTION ANALYSIS

Mathematical Procedure

The size distribution of fine particles in the Denver aerosol was assumed to be lognormal, having the following functional representation:

$$f(D) = \left\{\exp - \left[(\ln D - \ln D_a) / (2^{1/2} \ln \sigma)\right]^2\right\} / \left[(2\pi)^{1/2} D \ln \sigma\right], \quad (1)$$

where D is the aerodynamic diameter, D_a is the mass median aerodynamic diameter of the distribution, and σ is the distribution's geometric standard deviation. If the collection efficiencies $E_k(D)$ are known for all impactor stages k, the aerosol mass concentration deposited on stage i may be de-

TABLE 1. Characteristics of Microorifice Impactor

Stage name	Subscript (k)	Number of holes	Hole (diameter, μm)	Impaction surface
A	0	85	740	Greased aluminum
B	1	85	489	Teflon filter
D	2	2000	107	Teflon filter
F	3	2000	59	Teflon filter

termined from the equation,

$$F_i = M_T \int_0^\infty f(D) E_i(D) \prod_{k=0}^{i-1} [1 - E_k(D)]\, dD \Big/ \int_0^\infty f(D)[1 - E_o(D)]\, dD, \quad (2)$$

where the specific impactor stages are identified according to stage numbers in Table 1, and $i = 4$ pertains to the backup filter. The total measured mass concentration is M_T. The numerator in Eq. (2) has been described previously by Sundelof (1967) and Raabe (1978); we introduced the denominator to account for the fact that a portion of the aerosol is collected on the inlet stage 0, which is not analyzed. The efficiency of the backup filter was taken to be

$$E_4(D) = 1, \quad (3)$$

since the type of filter that we used has been shown to be essentially 100% efficient (Liu et al., 1983). The impactor efficiencies $E_k(D)$ for $k = 0$, 1, 2, and 3 were approximated by the formula

$$E_k(D) = a_k \left\{ b_k + (1 - b_k) \Big/ \left[1 + (d_k/D)^Z\right] \right\}, \quad (4)$$

where

$$Z = \left[1 + e_k(D - d_k)/d_k\right] p_k. \quad (5)$$

For each stage k, the collection efficiency is close to 50% for $D = d_k$, and the efficiency curve's steepness and skewness are represented by p_k and e_k, respectively. The stage's maximum efficiency is a_k, and its minimum efficiency is the product $a_k b_k$. To represent an ideal impactor that changes abruptly in efficiency from 0 to 100% at $D = d_k$, the following values would be chosen: $a_k = 1$, $b_k = e_k = 0$, and $p_k = \infty$. The actual values that we used are described in a later section.

The size distribution parameters, D_a and σ, were determined by a nonlinear least-squares method, which involves the expression

$$\chi^2 = \sum_{i=1}^{N} (F_i - M_i)^2 / \Delta M_i^2. \quad (6)$$

Here, M_i is the measured mass collected on stage i, ΔM_i is an estimate of the random portion of the measurement error for M_i, and N is the number of analyzed stages ($N = 4$ in the present study). The function F_i is given by Eq. (2) and depends on D_a and σ. The optimum values of D_a and σ are obtained by varying them iteratively until a minimum in χ^2 is reached.

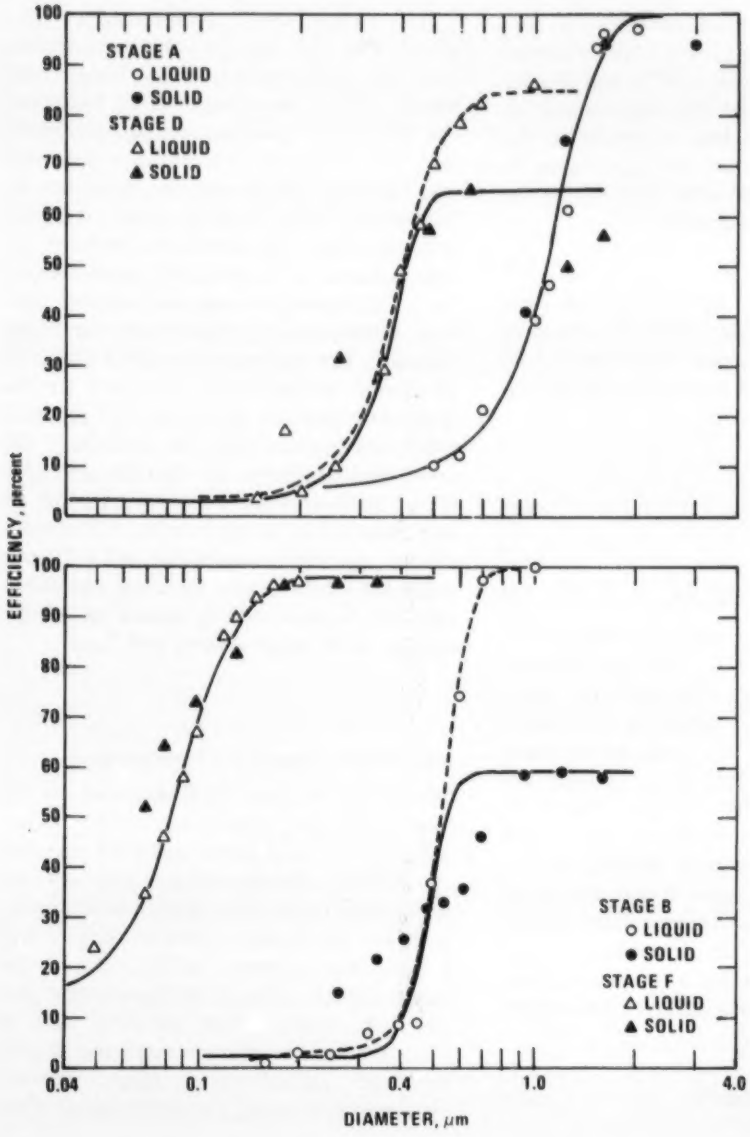
Two procedures for minimizing χ^2 were tested. The first one—a simplex minimization procedure developed by Nelder and Mead (1965)—was found to be inefficient for the present problem, because too many iterations were required before a minimum was reached. The second one, described by Bevington (1969), involved a gradient expansion algorithm; the procedure combines the best features of the gradient search method for χ^2 minimization with an analytical solution developed from linearizing the fitting function. The computer subroutine CURFIT developed by Bevington was used for the gradient expansion algorithm. We obtained rapid convergence with this procedure; the convergence criterion was that the new value of χ^2 differed from the previous value by less than 0.1%. In performing the computations, the integral appearing in Eq. (2) was computed numerically by using Simpson's rule for 77 steps equally spaced on a logarithmic scale between 0.001 and 7 μm.

Microorifice Impactor Characteristics

Marple and Rubow (1984) measured the collection efficiency of each microorifice impactor stage for both liquid and solid particles. A vibrating orifice aerosol generator was used to produce liquid (oleic acid) and solid (ammonium fluorescein) particles larger than 1 μm. Monodisperse submicrometer-sized liquid particles (dioctyl phthalate) were produced by using a fluid atomizer with an evaporation–condensation stage and an electrostatic classification stage. Submicrometer-sized solid particles (sodium chlo-

FIGURE 1. Collection efficiencies of microorifice impactor stages for liquid and solid particles. The points represent data obtained by Marple and Rubow (1984) and are reproduced with their permission. The smooth curves were calculated by using Eqs. (4) and (5) and the data of Table 2.

ride) were generated similarly, except that no evaporation–condensation stage was used. The results of Marple and Rubow for the collection surfaces that we used are plotted in Figure 1. The smooth curves in Figure 1 are based on Eqs. (4) and (5) and the param-



eters listed in Table 2 for liquid and solid particles.

The parameters for liquid particles were determined by an iterative search procedure that minimized the squares of the deviations from the measured points. Two features are apparent in the parameters for liquid particles. First, the maximum efficiency for stage D is only 85% (i.e., $a_2 = 0.85$). Marple and Rubow (1984) describe a physical basis for the lack of 100% efficiency for stage D, and they suggest design changes that could improve its performance. Second, for the stages that used Teflon membrane filters as impaction surfaces (stages B, D, and F), the collection efficiency was not zero for very small particles, and this required the parameters b_k to be nonzero.

To account for the lower air temperature (~ 0°C) and pressure (~ 840 mb) in Denver, we used the following expression to correct the impactor stages' characteristic diameters that were derived from laboratory conditions:

$$\left(d_k^2 C_k/\mu\right)_{\text{Denver}} = \left(d_k^2 C_k/\mu\right)_{\text{lab}}. \quad (7)$$

Here, C_k is the slip correction factor, which we computed from an expression by Friedlander (1977), and μ is the air viscosity. The resulting values of d_k for Denver are shown in Table 2.

In deriving parameters to describe the collection efficiencies for solid particles, we had to avoid the influence of two nonideal characteristics of the aerosol generation process. First, sodium chloride particles are nonspherical, which makes it difficult to relate their sizes to the diameters of aerodynamically equivalent spheres. Second, the sodium chloride aerosol was not completely monodisperse because an evaporation–condensation stage could not be included in the aerosol generator for solid particles. Polydispersion would cause the impactor's characteristic curves to appear less steep than they truly are. Indeed, the solid particle data plotted in Figure 1 exhibit a diameter bias and a lack of steepness when compared to the liquid particle data. We attributed these effects to the aerosol, not to the impactor.

Therefore, the solid particle data were used only to determine if particle bounce limited a stage's maximum efficiency. For stages A and F, there was no significant difference between the maximum efficiencies for liquid and solid particles, and we concluded that there was not a particle bounce problem. Hence, stages A and F have the same parameters for liquid and solid particles. For stages B and D, it appeared that particle bounce severely limited the efficiency for particle diameters above the 50% efficiency diameters. We determined the five parameters for stage B by the following procedure: b_1 was assumed to have the same value for solid particles and liquid particles, and a_1 was set at 0.59—the maximum efficiency for solid particles. The remaining three parameters were determined in an iterative search to obtain a best fit to the liquid particle data for which collection efficiency was less than 59%. The parameters for stage

TABLE 2. Parameters to Describe Efficiency Curves for Microorifice Impactor

	Solid Particles				Liquid particles			
Stage name	A	B	D	F	A	B	D	F
k	0	1	2	3	0	1	2	3
d_k, μm (lab.)	1.11	0.490	0.360	0.0875	1.11	0.545	0.395	0.0875
d_k, μm (Denver)	1.072	0.475	0.350	0.0872	1.072	0.528	0.384	0.0872
p_k (steepness)	4.9	13.0	8.0	4.4	4.9	10.5	5.6	4.4
e_k (skewness)	0.8	0.95	0.7	0.3	0.8	0.8	0.3	0.3
a_k (max. eff.)	1.00	0.59	0.65	0.98	1.00	1.00	0.85	0.98
b_k (zero bias)	0.00	0.02	0.04	0.12	0.00	0.02	0.04	0.12

D were determined in a similar manner; the value of a_2 was set at 0.65.

Criteria for Suitable Data

The method for deducing size distribution parameters is applicable only to data that have adequate precision. Moreover, the fact that the microorifice impactor that we used had only four stages in the fine particle range further limited its application to size distributions for which a fine particle mode was distinct. We found that meaningful results could be obtained when the following criteria were met:

$$M_i > 3\Delta M_i \text{ for at least three stages,} \quad \text{(C1)}$$

$$M_F > 0.5 M_C, \quad \text{(C2)}$$

$\Sigma M_i = M_F$ within measurement precision or within $\pm$ 25%, and (C3)

$$d_3 < D_a < d_0. \quad \text{(C4)}$$

Here, M_F and M_C pertain to concentrations of species in the fine ($D < 2.5$ μm) and coarse ($2.5 < D < 15$ μm) fractions, respectively, which were collected simultaneously in the adjacent dichotomous sampler.

The requirement of a minimal amount of precision is specified by criterion (C1). Criterion (C2) enables one to exclude cases for which the coarse particle mode is so large that its lower tail obscures the fine mode. Criterion (C3) enables one to exclude fine mode data having unrecognized poor precision or bias. (Here, it is implicitly assumed that there is little mass in the size range $1.1 < D < 2.5$ μm.) Cases for which D_a is outside of the impactor's range of determination are excluded by criterion (C4).

RESULTS

When we applied the gradient expansion algorithm to determine size distribution parameters for fine mode aerosol in Denver, we did not know whether to represent the impactor's efficiency curves by data for solid particles or liquid particles. Therefore, we made the calculations separately for each particle type. In addition, we made a set of calculations assuming an ideal impactor for which $b_k = e_k = 0$; $a_k = 1$; $p_k = 999$; and d_k has the values shown in Table 2 for liquid particles.

Tables 3 and 4 show detailed results for mass (S), potassium (K), bromine (Br), and lead (Pb) collected during the 11.5-h period beginning at 18:35 MST, January 12, 1982. Table 3 shows the measured masses and uncertainties for each impactor stage and demonstrates that their sums agree very well with dichotomous sampler results for fine particles. This indicates that the microorifice impactor deposits are sufficiently uniform for accurate XRF analysis. Fitted masses F_i are also shown in Table 3. Table 4 shows the derived values of D_a and σ. The uncertainties under the columns labeled CURFIT represent one standard deviation and were computed from the uncertainties in the species concentrations ΔM_i by using an algorithm that is included in subroutine CURFIT (Bevington, 1969). Table 5 shows values of D_a and σ that were averaged for the sampling periods that met the data acceptance criteria. Figure 2 shows time series plots of Pb and S concentrations and D_a values. The error bars were calculated from subroutine CURFIT in the manner indicated above. Before discussing these results, we first examined whether the data satisfied our acceptance criteria and whether the error estimates were valid.

The acceptance criteria were applied to 16 periods for which simultaneous microorifice impactor and dichotomous sampler measurements were made. The number of samples that failed the criteria were 0 for S, 6 for Br and Pb, 12 for mass and zinc, and 14 for K. All of the chlorine and iron data were rejected because a large coarse particle mode overwhelmed the fine mode; this resulted in a failure to satisfy criterion (C2). Much of the K data was rejected for the same reason. For mass, the concentrations were often so low compared to the measurement precision

TABLE 3. Concentrations Measured (M_i) for Impactor Stages and Dichotomous Sampler Compared with Least-Squares Fitted Values (F_i) for Samples Collected in Denver During the Night of January 12–13, 1982

	Unit	Parameter	$i=1$	$i=2$	$i=3$	$i=4$	ΣM_i	Dichotomous sampler	
								Fine	Coarse
Mass	$\mu g/m^3$	M_i	4.8	4.3	20.8	4.0	33.9	36	7
		F_i solid	4.0	5.3	20.4	4.3	33.9		
		F_i liquid	4.6	4.7	20.5	4.1	33.9		
		ΔM_i	1.2	1.2	1.7	2.0	3.1	3	3
S	ng/m^3	M_i	171	300	659	150	1280	1254	213
		F_i solid	188	220	732	140	1280		
		F_i liquid	184	187	779	129	1280		
		ΔM_i	12	20	51	16	58	95	187
K	ng/m^3	M_i	13	20	89	22	144	132	110
		F_i solid	13	20	89	22	144		
		F_i liquid	14	18	91	22	144		
		ΔM_i	2	2	5	2	6	8	16
Br	ng/m^3	M_i	16	19	127	51	213	207	41
		F_i solid	14	22	124	54	213		
		F_i liquid	15	20	125	52	213		
		ΔM_i	1	1	6	3	7	11	4
Pb	ng/m^3	M_i	41	54	352	153	600	638	154
		F_i solid	37	59	347	156	600		
		F_i liquid	41	55	351	154	600		
		ΔM_i	3	3	18	8	20	34	13

TABLE 4. Parameters for Fine Mode Denver Aerosol Deduced for Different Types of Impactor Curves for the Nighttime Sampling Period on January 12–13, 1982

	Type	D_a	ΔD_a, nm			σ	$\Delta\sigma$			$\chi^2/2$
		nm	CURFIT	*M*C1	*M*C2		CURFIT	*M*C1	*M*C2	
Mass	Solid	245	37	44	49	2.33	0.33	0.35	0.37	0.6
	Liquid	224	30	35	38	2.13	0.24	0.25	0.27	0.1
	Ideal	241	30			2.41	0.25			0.1
S	Solid	289	15	16	44	2.46	0.15	0.17	0.29	10
	Liquid	239	8	9	22	2.06	0.08	0.09	0.17	20
	Ideal	246	8			2.36	0.08			34
K	Solid	208	11	10	14	2.26	0.12	0.10	0.16	0.1
	Liquid	191	8	8	11	2.06	0.09	0.07	0.13	1.0
	Ideal	203	9			2.34	0.09			6.0
Br	Solid	151	5	4	8	2.45	0.09	0.10	0.20	6.1
	Liquid	145	4	4	6	2.24	0.07	0.07	0.18	1.2
	Ideal	164	4			2.47	0.06			6.1
Pb	Solid	146	4	4	7	2.44	0.09	0.12	0.19	2.2
	Liquid	139	4	3	7	2.23	0.07	0.08	0.21	0.1
	Ideal	157	4			2.49	0.07			9.0

TABLE 5. Mean Values of D_a and σ for the Fine Mode of Denver Aerosol Assuming both Liquid- and Solid-Type Particles[a,b]

Species	Number of samples	Solid particles		Liquid particles	
		D_a, nm	σ	D_a, nm	σ
Mass	5	316(180) ± 193	3.1(1.6) ± 1.3	215(38) ± 36	2.4(0.7) ± 0.4
S	17	261(101) ± 18	2.2(0.4) ± 0.1	223(53) ± 9	1.9(0.3) ± 0.1
S	11[c]	249(57) ± 12	2.2(0.3) ± 0.1	216(32) ± 8	1.9(0.2) ± 0.1
Br	11[c]	163(38) ± 10	2.7(0.5) ± 0.2	148(22) ± 6	2.4(0.3) ± 0.1
Pb	11[c]	143(14) ± 5	2.6(0.3) ± 0.1	135(13) ± 4	2.3(0.2) ± 0.1

[a] Standard deviations are in parentheses.
[b] The ± values are averages of the uncertainties computed by subroutine CURFIT.
[c] The 11 sampling periods are those for which the Pb concentration exceeded 100 ng/m³ (see Figure 2).

shown in Table 3 that in 11 instances criterion (C1) was not satisfied, and in one instance (C3) was not satisfied. Failure to satisfy criterion (C1), (C3), or (C4) in instances of low species concentrations relative to measurement precision was the most common reason for rejecting data for Zn, Br, and Pb. In every case for which the Br and Pb data were rejected, the Pb concentration was below 100 ng/m³; to facilitate identification of those cases, a horizontal line representing 100 ng/m³ was plotted in Figure 2. Thus, there were 11 sampling periods for which the Br and Pb results were valid and can be compared with results for *S*.

Uncertainty Estimates

Because the algorithm used to compute the error estimates is an approximation when nonlinear expressions such as Eq. (2) are used (Bevington, 1969), we computed the uncertainties by a Monte Carlo method. In the Monte Carlo method, 50 normally distributed random numbers were generated for the mass on each impactor stage such that the mean was M_i and the standard deviation was ΔM_i. Here, M_i and ΔM_i represent the measured masses and uncertainties as in Eq. (6). The data for M_i and ΔM_i used in our calculations were obtained for the nighttime sample collected on January 12–13. Each of the resulting 50 sets of random impactor "data" was analyzed by the gradient expansion algorithm to yield 50 pairs of values for D_a and σ. Their standard deviations, ΔD_a and $\Delta\sigma$, were computed and are shown in Table 4 under the columns labeled *M*C1.

The differences between the standard deviations *M*C1 and those obtained by subroutine CURFIT were generally fairly small and arose partly from the statistical variability associated with the Monte Carlo method. If the differences could be attributed only to randomness of our sample consisting of 50 sets of submitted data, the ratio of the CURFIT and *M*C1 estimates would fall in the range 0.83 to 1.237 for 97% of all cases (Natrella, 1963). However, only 80% of the ΔD_a estimates and 80% of the $\Delta\sigma$ estimates shown in Table 4 fall within that range. This indicates that the two types of error estimates are not strictly equivalent. However, the smallness of the differences and the 50 times greater computational cost required for the Monte Carlo method suggest that the error estimates made by subroutine CURFIT are both acceptable and economical.

The error estimates discussed above do not include the uncertainty of the impactor's characteristics. Hence, they are only useful for determining the significance of differences in the size distributions for different time periods or different chemical species collected in the same cascade impactor.

To determine an overall uncertainty in D_a and σ caused by uncertainty in the input data M_i, d_k, and p_k, we again used a Monte Carlo method. We assumed that the stan-

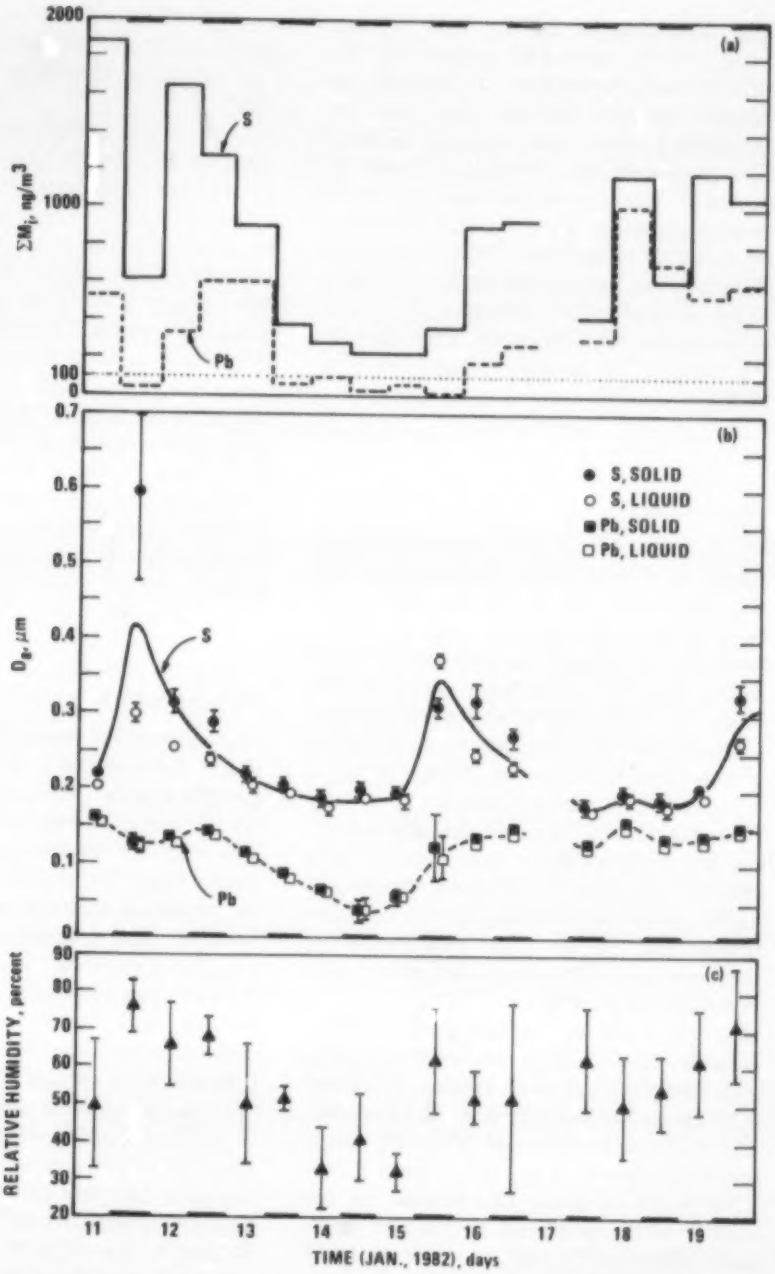


FIGURE 2. Time series plots of relative humidity, fine mode concentrations, and D_a values for Pb and S in Denver aerosol. For relative humidity, the bars represent one standard deviation about the mean of the data during each 12-h interval.

dard deviations of d_k, p_k, and M_i were 0.1 d_k, 0.2 p_k, and ΔM_i, respectively. For each of these parameters, 50 normally distributed random numbers that have the parameter's mean and standard deviation were generated; then 50 pairs of values for D_a and σ were determined from the 50 sets of simulated data. Their standard deviations are assumed to represent the overall uncertainties in D_a and σ, and they are listed in Table 4 under the columns $MC2$. As expected, the $MC2$ errors are larger than the $MC1$ errors. The increases range from 10 to 175%.

DISCUSSION

The data in Tables 4 and 5 show that the D_a values for Denver's fine mode aerosol were very similar for Br and Pb; Br values were larger by a barely significant amount. Such a similarity is expected because both Pb and Br are emitted by the same source, the exhaust of vehicles fueled by leaded gasoline. On the other hand, the average D_a value for S was larger than that for Pb by a factor of 1.7, and the D_a for S varied independently from that for Pb. This indicates that individual fine particles differ from each other in composition. Such a conclusion was reached earlier in an examination of the humidity dependence of the size distribution of Denver's aerosol during December 1978 (Countess et al., 1981).

In the study by Countess et al. (1981), a cascade impactor with grease-coated stages was used to obtain the following D_a values: 0.34 μm for ammonium, 0.36 μm for sulfate, and 0.25 μm for bromide. These D_a values are larger than ours in Table 5 for S and Br by a factor of about 1.6. Because the two studies were conducted at different times, such differences could represent real differences in the aerosol. The differences between the present results and those of Countess et al. (1981) are certainly larger than our error estimates, and they are larger than the 10 to 16% ambiguity in our average results for S and Br that results from different collection efficiencies for liquids and solids.

One cannot definitively say whether the sampled S behaved as a liquid or a solid. On the one hand, values of χ^2 were lowest when the particles were assumed to behave as solids. On the other hand, the relative humidity (RH) data in Figure 2 show that RH sometimes exceeded 80%. At this value, ammonium sulfate would be a liquid; acid ammonium salts would be a liquid at even lower RH (Tang, 1980). For example, during the night of January 11–12, D_a for S was deduced to be 0.3 μm if the particles were liquid and 0.6 μm if they were solid. The possibility that the S behaved only as solid particles can be rejected because the RH exceeded 80% for a portion of that sampling period.

CONCLUSIONS

The microorifice impactor was shown to be useful for collecting size-fractionated fine particle samples. The sum of concentrations for the impactor stages below 1.1 μm agreed well with fine fraction dichotomous sampler results for S, Pb, and Br. This indicates that the impactor deposits are sufficiently uniform so that quantitatively XRF analysis can be performed. Twelve-hour sampling periods often resulted in insufficient sample for mass and zinc. Species such as chlorine, potassium, and iron often had a large coarse particle mode whose lower tail interfered with the fine particle mode.

We have developed a procedure for fitting lognormal distribution functions to cascade impactor data that enables one to determine both the magnitudes and the uncertainties of D_a and σ. The relatively rapid algorithm for estimating uncertainties caused by measurement error in impactor stage mass was shown to be in good agreement with results from a more time-consuming and expensive Monte

Carlo method. Our D_a values for the fine mode S and Br were smaller by a factor of about 1.6 than values obtained by means of a cascade impactor by Countess et al. (1981) in Denver during 1978. Because liquid and solid particles were collected with different efficiencies on two of the impactor stages that we used, the average values of D_a deduced for S, Br, and Pb were ambiguous by 16, 10, and 6%, respectively. Moreover, the ambiguity in collection efficiency greatly complicated the task of analyzing and interpreting the data. To avoid or reduce such complication in future applications of the microorifice impactor, it is suggested that all impaction surfaces be coated with grease. Also, in future studies the impactor stages should have cutoff diameters that are more uniformly spaced than the ones we used.

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